Method for deducing anisotropic spin-exchange rates

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Using measured spin-transfer rates from alkali-metal atoms to ^{3}He, combined with spin-relaxation rates of the alkali-metal atoms due to ^{3}He and ^{4}He, it should be possible to differentiate between isotropic and anisotropic spin exchange. This would give a fundamental limit on the ^{3}He polarization attainable in spin-exchange optical pumping. For K-He, we find the limit to be 0.90 ± 0.11.

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I. INTRODUCTION AND MOTIVATION

The spin-dependent interactions governing spin-exchange collisions between alkali-metal atoms and noble-gas atoms are [1]

$$V = \alpha(R)\mathbf{S}\cdot\mathbf{K} + \beta(R)(3\mathbf{S}\cdot\hat{\mathbf{R}}\hat{\mathbf{R}}\cdot\mathbf{K} - \mathbf{S}\cdot\mathbf{K}), \tag{1}$$

where α is the strength of the Fermi contact or isotropic hyperfine interaction between the alkali-metal electron spin $\mathbf{S}$ and the noble-gas nuclear spin $\mathbf{K}$, and β is the strength of the anisotropic hyperfine interaction. Both α and β depend on the interatomic separation $\mathbf{R}$.

Anisotropic spin exchange was recently considered by Walter *et al.* [2] and, on the basis of theoretical arguments that have generally been successful in explaining the size of various alkali-metal–noble-gas spin interactions, was found to be a small effect. If present, anisotropic spin exchange would modify the dynamics of polarization transfer from an alkali-metal vapor of number density $[A]$ to the helium nucleus to [2,3]

$$\frac{dP_{\mathrm{He}}}{dt} = k_\alpha[A](P_A - P_{\mathrm{He}}) + k_\beta[A]\left(-\frac{P_A}{2} - P_{\mathrm{He}}\right) - \Gamma_w P_{\mathrm{He}}, \tag{2}$$

where k_α and k_β are the rate coefficients arising from the two interactions and Γ_w represents depolarization from diffusion through magnetic field gradients and from relaxation at the wall of the gas enclosure. Note that anisotropic spin exchange tends to polarize the He nuclei in the direction opposite that of the alkali-metal polarization. In the presence of completely polarized alkali-metal vapor and nonrelaxing walls, nearly achievable in practice, the anisotropic interaction would limit the maximum attainable polarization to

$$P_{\max} = \frac{k_\alpha - k_\beta/2}{k_\alpha + k_\beta}. \tag{3}$$

Walter *et al.* [2] predicted $P_{\max} = 0.96$ for Rb-^{3}He and 0.95 for K-^{3}He. Extensive experiments at University of Wisconsin and National Institute of Standards and Technology (NIST) [3–5] have shown that some unknown spin-relaxation mechanism limits the ^{3}He polarization, even under supposedly ideal conditions, to less than 80% for both Rb and K-Rb mixtures. Could one source of this relaxation be anisotropic spin exchange? Here we present a method for experimentally answering this question by deducing k_β from spin-exchange and alkali-metal spin-relaxation measurements.

II. LIMITS FROM WALL-RELAXATION STUDIES

The approach of P_{He} to saturation in the presence of a polarized alkali-metal vapor can be experimentally characterized by its saturation level P_{He}^∞ and rate of approach to saturation Γ. From Eq. (2),

$$P_{\mathrm{He}}^\infty = P_A\frac{(k_\alpha - k_\beta/2)[A]}{\Gamma_w + (k_\alpha + k_\beta)[A]}, \tag{4}$$

$$\Gamma = \Gamma_w + (k_\alpha + k_\beta)[A]. \tag{5}$$

For any given measurement $P_{\mathrm{He}}(t)$ performed at constant $P_A[A]$, Γ_w can be eliminated, leaving

$$k_\alpha - k_\beta/2 = \frac{P_{\mathrm{He}}^\infty\Gamma}{[A]P_A}. \tag{6}$$

The quantity $k_{\mathrm{SE}} = k_\alpha - k_\beta/2$ is what is observed in recent spin-exchange measurements [3,5,6]. It might appear that measurements of P_{He}^∞ or Γ as a function of $[A]$ would allow determination of $k_\alpha + k_\beta$. However, it is now well established [3,5] that Γ_w depends strongly on $[A]$, making this approach not feasible.

The latest wall studies [5], surveying many cells having a range of surface-to-volume ratios S/V, found that the observed maximum polarization is well described by

$$\frac{P_{\mathrm{He}}^\infty}{P_A} = \frac{1}{1+X}, \tag{7}$$

where X is of the form

$$X = X_0 + X_1\frac{S}{V}. \tag{8}$$

If we assume that X_0 represents the fundamental (wall-independent) effects of the anisotropic hyperfine interaction, comparison to Eq. (3) yields

$$X_0 = \frac{3k_\beta}{2k_\alpha - k_\beta}. \tag{9}$$

The factor X_0, which would represent a limit on P_{He} from collisions in the gas, could be as small as 0 and as large as 0.15 [5]. The measured X_1 values vary substantially from cell to cell, presumably due to its very sensitive dependence on the

exact physical and chemical nature of the wall, and therefore limit the certainty of the results.

III. METHOD

Our basic idea is to determine $k_\alpha + k_\beta$ by comparing spin-relaxation measurements of alkali-metal atoms in ^{3}He and ^{4}He. The spin-relaxation rate of the alkali-metal atoms due to ^{3}He is, at low polarization and low-enough temperatures that the alkali-metal–alkali-metal spin-relaxation rates can be ignored,

$$^3\gamma_A = {}^3k[^3\mathrm{He}] = \left({}^3k_{SR} + k_\alpha + k_\beta\right)[^3\mathrm{He}], \tag{10}$$

where k_{SR} is the relaxation produced by the spin-rotation interaction. The spin-relaxation rate due to ^{4}He is simply

$$^4\gamma_A = {}^4k_{SR}[^4\mathrm{He}], \tag{11}$$

since there is no spin-exchange for ^{4}He. Thus, we can use the relaxation of the alkali-metal atoms in ^{4}He gas to isolate the spin-exchange and spin-relaxation contributions. We argue later on this article that the spin-relaxation rates for the two isotopes scale linearly with the collision velocities, so that

$$^3k_{SR} = \sqrt{\frac{\mu_4}{\mu_3}}\,{}^4k_{SR}, \tag{12}$$

where μ is the reduced mass of the He–alkali-metal pair. This scaling should allow us to separate the spin-exchange and spin-rotation contributions to the alkali-metal spin-relaxation rate:

$$k_\alpha + k_\beta = {}^3k - \sqrt{\frac{\mu_4}{\mu_3}}\,{}^4k_{SR}. \tag{13}$$

Thus subtracting the scaled ^{4}He spin-relaxation rate from the ^{3}He spin-relaxation rate isolates the sum of the isotropic and anisotropic spin-exchange rates.

Experimentally, the challenge is to measure the alkali-metal spin-relaxation rates carefully enough to preserve significance for the subtraction in Eq. (13). The Rb-^{3}He spin-exchange rate has now been measured by two different groups [3,6] to be 6.8×10^{-20} cm^3/s. The relaxation rates for Rb-He are unfortunately about 16–50 times bigger (depending on temperature) than the spin-exchange rates. Thus very-high-precision measurements would need to be made.

The situation is much better for potassium, where the measured efficiencies suggest a factor of 10 more favorable ratio of spin-exchange to spin-relaxation rates.

We now turn to the scaling relation for the two isotopes. The spin-rotation coupling $\gamma(R)$, R being interatomic separation, is inversely proportional to the reduced mass μ of the colliding pair. This is because the rotation frequency of the atoms about each other is

$$\boldsymbol{\omega} = \frac{\hbar \mathbf{N}}{\mu R^2}, \tag{14}$$

which give rise to a Coriolis interaction,

$$V_\omega = -\hbar\boldsymbol{\omega}\cdot\mathbf{L}, \tag{15}$$

where $\mathbf{L}$ is the electronic angular momentum [7]. The spin-rotation coupling then arises due to the response of the electron to the effective magnetic field $B = \hbar\omega/(g_S\mu_B)$. Thus, one expects on very general grounds that $\gamma(R) \propto 1/\mu$.

The spin-relaxation rate coefficient is an average over the possible collision trajectories [8],

$$k_{SR} = \frac{8\pi\bar{v}\mu^2}{3\hbar^2}\int_0^\infty we^{-w}dw\int_0^\infty b^3db \times \left|\int_{r_o}^\infty \frac{\gamma(R)dR}{\sqrt{(1-b^2/R^2)-V(R)/wkT}}\right|^2, \tag{16}$$

where w is a dimensionless variable and b the impact parameter of the collision. $V(R)$ is the Rb-He potential, which should be very insensitive to the mass of the He nucleus. The inverse scaling of γ with reduced mass cancels the μ^2 factor in front of the integrals so that the mass dependence of the spin-relaxation rate coefficient arises entirely from the relative velocity factor $\bar{v} \propto 1/\sqrt{\mu}$.

IV. EXPERIMENT

The K-He spin-relaxation measurements were made at Amersham Health using a 7.1-cm-diameter spherical-valved cell containing K metal with a very small amount of Rb metal dissolved in it. The Rb vapor density was measured to be $2 \pm 0.4 \times 10^{-3}$ that of the K. The Rb atoms were polarized to typically 20% polarization (parallel to a 20-G magnetic field) by optical pumping with a 60-W diode laser. The polarized Rb atoms then polarized the K atoms by spin-exchange collisions. A mechanical shutter periodically blocked the laser light to allow the alkali-metal polarization to decay due to spin-relaxation.

A single-frequency tunable diode laser, operating at typically 3 nm or more from the potassium D_1 line at 770 nm, was used to monitor the spin polarization of the alkali-metal atoms by Faraday rotation. The spin-relaxation transients were then analyzed to extract the slowest decay mode of the relaxing atoms. This procedure was repeated a number of times as the pressure and composition of the cell was varied. Two decays were taken at each pressure, with different probe laser intensities. A linear extrapolation to zero probe-laser intensity was performed to remove the effect of the probe laser (at most a 5% correction).

Three gases were used for the experiments. The "^{3}He" gas was actually a 0.9922:0.0078 ^{3}He-N_2 mixture that was the standard Amersham gas mixture. Pure nitrogen gas was also used so that the nitrogen contribution to the ^{3}He relaxation could be corrected for. The third gas was ^{4}He. The cell was filled with the gas of interest at high pressure. Immediately after filling with the fresh gas, the alkali-metal vapor pressure would suddenly drop, then slowly recover over the period of about an hour. The drop in pressure was presumably due to chemical reactions with impurities in the gases. To vary the gas pressure, hot gas was pumped out through the cell valve. Since this was done with the cell hot, the gas density was determined from the pressure using the ideal gas law at the 150°C cell temperature.

The measured spin-relaxation decay rates are shown in Fig. 1. On a given day, the data vary smoothly with pressure; however, we found some systematic day-to-day changes that are outside normal statistical fluctuations. For example, the ^{3}He data points at 6.9 and 2.9 amagat were taken on different

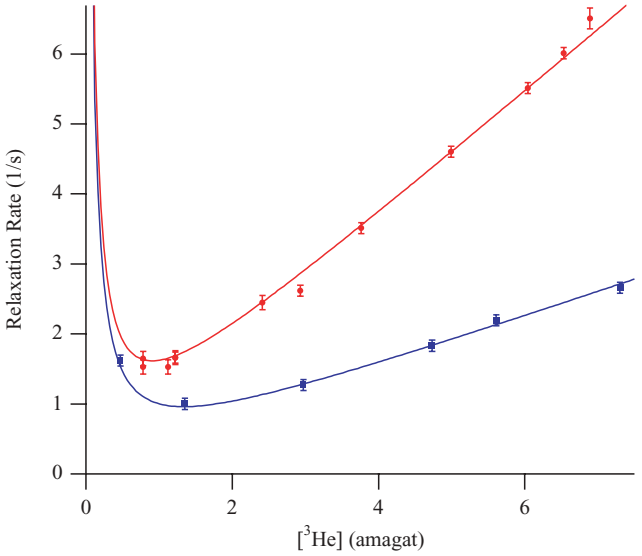

FIG. 1. (Color online) Spin-relaxation data for K in two gas mixtures. The circles represent the ^{3}He-N_2 mixture; the squares pure ^{4}He. The error bars are the standard deviations in the relaxation rates deduced from the polarization transients.

days than most of the other data. The size of these unexplained fluctuations is about 4%.

V. ANALYSIS

The data for the two gases were fit to the following function:

$$\Gamma = D_0\sqrt{\frac{\mu_3}{\mu_G}}\left(\frac{\pi}{R}\right)^2\frac{1\ \text{amagat}}{[G]} + \Gamma_0 + k[G], \tag{17}$$

with the first term representing diffusion to the cell walls, the second K-K relaxation, and the third spin-relaxation due to K-G collisions. Based on S. Kadlecek's thesis [9], we expect $\Gamma_0 < 0.1$/s at this temperature and this parameter was actually taken to be zero for the fit. The data for both gases were fit simultaneously, assuming that the diffusion coefficient scales inversely with the square root of the reduced mass μ of the K-G pair. Thus, only three parameters, D_0, $k(^3\text{He})$, and $k(^4\text{He})$, were used to fit the entire data set. The results are

$$\begin{aligned} D_0 &= 0.91 \pm 0.04\ \ \text{cm}^2/\text{s} \\ k(^3\text{He}) &= 0.89 \pm 0.040/\text{s amagat} \\ k(^4\text{He}) &= 0.36 \pm 0.014/\text{s amagat}, \end{aligned} \tag{18}$$

with the error bars reflecting the unexplained day-to-day fluctuations in the results.

At the 150°C temperature, the K and Rb atoms are well into the regime where the spin-exchange rates between the alkali-metal atoms greatly exceed the spin-relaxation rates for the atoms. Thus, the atoms should be well described by a spin temperature. The presence of the Rb vapor at a concentration of 1/500 slightly modifies the usual slowing-down factor (which accounts for the flywheel effect of the alkali-metal nuclear spin [10]) of 6 for a nuclear spin-3/2 atom like K to $s = 6 + 10.8/500 = 6.02$. We also must account for a slight amount of Rb-He spin relaxation, measured by Baranga *et al.* [6] to be 41.2/s amagat for Rb^{3}He and, using the mass scaling, 36.1/s amagat for ^{4}He. We therefore find

$$\begin{aligned} {}^4k_{\text{SR}} &= s \times 0.36 - 36.1/500 = 2.10/\text{s amagat} \\ &= 7.8 \pm 0.4 \times 10^{-20}\ \text{cm}^3/\text{s} \end{aligned} \tag{19}$$

and, using the mass scaling,

$$\begin{aligned} {}^3k_{\text{SR}} &= 1.14\,{}^4k_{\text{SR}} = 2.39/\text{s amagat} \\ &= 8.9 \pm 0.4 \times 10^{-20}\ \text{cm}^3/\text{s}. \end{aligned} \tag{20}$$

These are the first measurements of spin relaxation of K by He.

Since the ^{3}He gas is actually a mixture, a correction for N_2 must also be made. From Ref. [9], and confirmed by a measurement at 28 psi (gauge), we find that nitrogen contributes 1.24/s amagat for the 0.78% mixture used. We therefore find for the total K-^{3}He spin-destruction rate coefficient (spin exchange plus spin rotation)

$${}^3k = s \times 0.89 - 1.24 - 41.2/500 = 4.04/\text{s amagat}. \tag{21}$$

The spin-exchange contribution is therefore

$$\begin{aligned} k_\alpha + k_\beta &= {}^3k - {}^3k_{\text{SR}} = 1.65/\text{s amagat} \\ &= 6.1 \pm 0.7 \times 10^{-20}\ \text{cm}^3/\text{s}. \end{aligned} \tag{22}$$

The latest measurements of k_{SE} [11] give $k_\alpha - k_\beta/2 = 5.5 \pm 0.2 \times 10^{-20}$ cm^3/s. Therefore, the X factor due to anisotropic spin exchange is

$$X_0 = \frac{6.1 \pm 0.7}{5.5 \pm 0.2} - 1 = 0.11 \pm 0.13. \tag{23}$$

This in turn implies that spin exchange using K-^{3}He collisions is fundamentally limited to a ^{3}He polarization of

$$P_{\text{max}} = \frac{1}{1 + X_0} = 0.90 \pm 0.11. \tag{24}$$

This result, though it does not rule out $P_{\text{max}} = 1$, is tantalizing since it suggests there may actually be a fundamental contribution to the X factor. Higher-precision measurements of both the spin-exchange rate coefficient and the spin-relaxation measurements are needed to reach a definitive conclusion.

We can combine our ^{3}He spin-relaxation results with k_{SE} to obtain a spin-exchange efficiency:

$$\eta = \frac{k_{\text{SE}}}{{}^3k} = \frac{5.5 \pm 0.2}{15.0 \pm 0.7} = 0.37 \pm 0.02. \tag{25}$$

This is in slight disagreement (1.25σ) with the Baranga *et al.* result [6] of 0.295 ± 0.06, which was in turn found to be consistent with our previous observations of the efficiency of hybrid spin exchange [12].

We note that the ITAMP group [13] is currently extending their *ab initio* calculations of spin-exchange parameters [14] to include the anisotropic contribution to spin exchange. Having reliable theoretical calculations would be very useful for both K and Rb, but especially for Rb, where it will be extremely difficult to experimentally deduce k_β.

We have presented in this article a method for isolating the anisotropic hyperfine interaction from the much larger isotropic hyperfine interaction for alkali-metal atoms interacting with ^{3}He. This issue is not only of interest for fundamental reasons; it has practical importance for maximizing the

attainable polarization in spin-exchange optical pumping. Considerable effort at NIST and Wisconsin [5] has gone into trying to improve the wall-relaxation performance of ^{3}He spin exchange. The best polarization observed to date is 81%. If this value is approaching the fundamental limit for the process, there is little to be gained through further laborious wall studies. On the other hand, if the limit is 95% or higher, there is room to substantially improve the performance of spin-exchange pumped targets for applications such as neutron spin filters [15], magnetic resonance imaging [16], and electron scattering [17].

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